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DETERMINATION OF ^{243}Am IN ^{244}Cm BY GAMMA SPECTROSCOPY

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DISCLAIMER

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ABSTRACT

Gamma spectroscopy with a high resolution Ge(Li) detector is used to determine ^{243}Am by its 74.7-keV gamma transition in solutions containing much higher specific activities of other actinides and fission products. As little as 250 ppm of ^{243}Am relative to ^{244}Cm can be determined. A relative standard deviation of 1.4% was obtained for routine samples. The method is well suited for analytical control of curium process steps because of its simplicity, speed, and reliability.

INTRODUCTION

A simple, rapid method was needed to determine ^{243}Am in curium process solutions during the separation and purification of 5 kilograms of ^{244}Cm at the Savannah River Laboratory. Available methods for determining ^{243}Am in the presence of high concentrations of ^{244}Cm are too slow, complicated, or insensitive for routine use in a production operation (1-5). A gamma counting method was developed that can be performed rapidly on a routine basis to determine ^{243}Am in solutions containing varying amounts of ^{244}Cm, other actinides, and fission products. The method is unaffected by highly salted, corrosive, or organic media. The ^{243}Am is determined by gamma spectroscopy with a lithium-drifted germanium, Ge(Li), semiconductor detector to resolve the 74.7-keV gamma ray (0.85 photons per

disintegration). Gamma spectroscopy is advantageous for analysis of ^{243}Am in the presence of ^{244}Cm because of the low abundance of gamma transitions from ^{244}Cm (1.5 x 10^{-5} photons per disintegration at 99 keV) (6).

EXPERIMENTAL

Apparatus. The Ge(Li) detector used for this analysis is a modified coaxial detector purchased from Nuclear Diodes, Inc. The resolution of this system is about 1.8 keV full width at half maximum (FWHM) at 74.7 keV. The detector efficiency is 1.5% (relative to a 3" x 3" NaI detector) at 20 cm for a 1332-keV gamma ray. The electronic system consists of a Tennelec TC 135L preamplifier, a Tennelec TC 200 linear amplifier, and a Nuclear Data 4096 channel pulse-height analyzer. The memory can be read out onto magnetic tape or printed out directly from a high speed Franklin printer.

Reagents. The counter was calibrated with a ^{243}Am solution (1.646 x 10^6 dpm/ml) that was standardized by isotope dilution-mass spectrometry, alpha counting and pulse-height analysis, and coulometry.

Procedure. Aliquots of the ^{243}Am standard and samples are pipetted into separate gamma counting tubes (8 ml glass vial with plastic cap) and diluted to 5 ml with 1M HNO$_3$ or a suitable solvent if the sample is organic. The tube is capped, sealed with plastic tape, and placed in a polystyrene vial (13/16-in.-OD x 3-5/8 in.-length) that is then capped and sealed with plastic tape. The standard and the sample are counted with the Ge(Li) detector in a holder which ensures reproducible geometry at 2 cm.

A gain setting of the amplifier is adjusted to provide a peak width of 10 channels (FWHM) to allow reliable integration of the photopeak area (7). For a Gaussian distribution, 99% of a peak area

is contained in 2.1 x (FWHM), but the actual Ge(Li) photopeak is not perfectly Gaussian. The peak width actually containing 99% of the peak area is approximately 2.4 x (FWHM) (8). Therefore, a peak area of 24 channels is used with a gain setting giving 10 channels (FWHM).

The contribution of underlying continuum background to this integrated photopeak area is assumed to be linear over the peak area. An average of the counts from 4 channels on each side of the peak is used for the average counts per channel from continuum background. This background is subtracted from the peak sum to obtain the net area of the photopeak. For a good analysis, the peak channel should contain at least 1000 counts more than the average counts per channel from continuum background.

RESULTS AND DISCUSSIONS

Accuracy and Precision. A comparison of ^{243}Am results obtained by gamma spectroscopy and isotope dilution-mass spectrometry showed that the gamma method was free from bias. Results are shown in Table I.

The precision of the analysis was studied under various conditions. The influence of these conditions can be seen in Table II. To determine the reproducibility of the pulse-height analyzer, an ^{243}Am sample was counted repeatedly without repositioning for four times the normal sample counting time. Then a sample that contained no significant interferences was run with repeated preparation of the sample and calibration of the detector. Another sample that contained only 0.2% ^{243}Am in ^{244}Cm with strong interferences from ^{144}Ce and ^{243}Cm was run with multiple preparation of the sample. With interferences, the precision was poorer, but no bias was observed when the results were compared to those obtained by the ^{239}Np extraction method (2).

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The reliability of the method was further verified with ^{243}Am-spiked samples. A sample containing ^{244}Cm and ^{243}Am (3.93 x 10^4 dpm) was analyzed with and without varying amounts (1.45 x 10^4 to 1.16 x 10^5 dpm) of ^{243}Am added. The average difference between the calculated and measured spike quantities was 4.5%.

LIMITATIONS AND INTERFERENCES

The technique is limited by the resolution of the detector and the accuracy of the correction for continuum background under the photopeak. Any gamma emitting nuclide with gamma rays above 74.7 keV can interfere with the analysis if the continuum counts from these gammas mask the photopeak.

A more difficult situation occurs when a gamma emitting nuclide is present that perturbs the continuum distribution under the photopeak. This interference has been observed with samples that contain ^{144}Ce, ^{243}Cm, and ^{239}Np. Figure 1 shows the proximity of the 80.1-keV ^{144}Ce peak to the ^{243}Am photopeak. The resolution of our detector is adequate to resolve the two peaks. Care must be taken to accurately correct for ^{144}Ce contribution to the photopeak to prevent a bias in the analysis. With the peak integration procedure described, the possible bias is less than 10% provided the ^{144}Ce peak is no greater than twice the intensity of the ^{243}Am peak. When the ^{144}Ce peak is greater than twice the ^{243}Am peak, the ^{144}Ce can be removed chemically to determine ^{243}Am (9,10).

The nuclides ^{243}Cm and ^{239}Np both decay into levels of ^{239}Pu and have similar gamma spectra. Their gamma spectrum has a shoulder (Fig. 1) just at the ^{243}Am photopeak. The method adopted for defining the background, which uses only 0.4 (FWHM) on each side of the photopeak, minimizes the inclusion of counts from this shoulder area in the ^{243}Am photopeak.

The sensitivity of this technique for ^{243}Am in pure ^{244}Cm is at least 100 ppm. In practice, all reactor-produced curium contains some ^{243}Cm which increases the Compton background; the best sensitivity achieved is about 250 ppm for curium that contains 0.02% ^{243}Cm.

APPLICATION

The gamma spectroscopic method has been applied successfully to routine samples. Average time for duplicate standardization and analysis of duplicate samples is 1.5 hr.

This technique can also be used to determine the ^{243}Am/^{244}Cm ratio by measuring the ^{243}Am peak and the ^{244}Cm peak at 42.9 keV. The relative counting efficiencies of these two photopeaks are obtained by counting standard mixtures of the nuclides. Figure 1 shows a spectrum of a sample containing 1.5% ^{243}Am in ^{244}Cm. This technique is particularly useful when it is difficult to obtain a representative sample because of solids, salts, etc. As long as the sample itself is homogeneous, a good analysis can be obtained. It is a particularly convenient technique for process control because it is insensitive to pipetting errors or errors such as counting time or sample positioning.

CREDIT

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TABLE I

COMPARISON OF MASS SPECTROMETRIC AND
SPECTROSCOPIC METHODS

Sample	^{243}Am, mg/ml Mass Spec.	Ge(Li)	Diff., %
1	4.01×10^{-4}	3.90×10^{-4}	-2.74
2	3.98×10^{-4}	4.15×10^{-4}	+4.27
3	4.01×10^{-4}	4.03×10^{-4}	+0.50
4	4.01×10^{-4}	3.80×10^{-4}	-5.24
5	1.16×10^{-3}	1.19×10^{-3}	+2.59
6	1.16×10^{-3}	1.09×10^{-3}	-6.03
7	1.17×10^{-3}	1.15×10^{-3}	-1.71
8	1.17×10^{-3}	1.13×10^{-3}	-3.42
9	1.36×10^{-3}	1.36×10^{-3}	0.00
10	1.36×10^{-3}	1.32×10^{-3}	-3.00
11	1.36×10^{-3}	1.40×10^{-3}	+3.00
12	1.35×10^{-3}	1.30×10^{-3}	-3.70

TABLE II

PRECISION OF ^{243}Am ANALYSIS BY Ge(Li) GAMMA SPECTROSCOPY

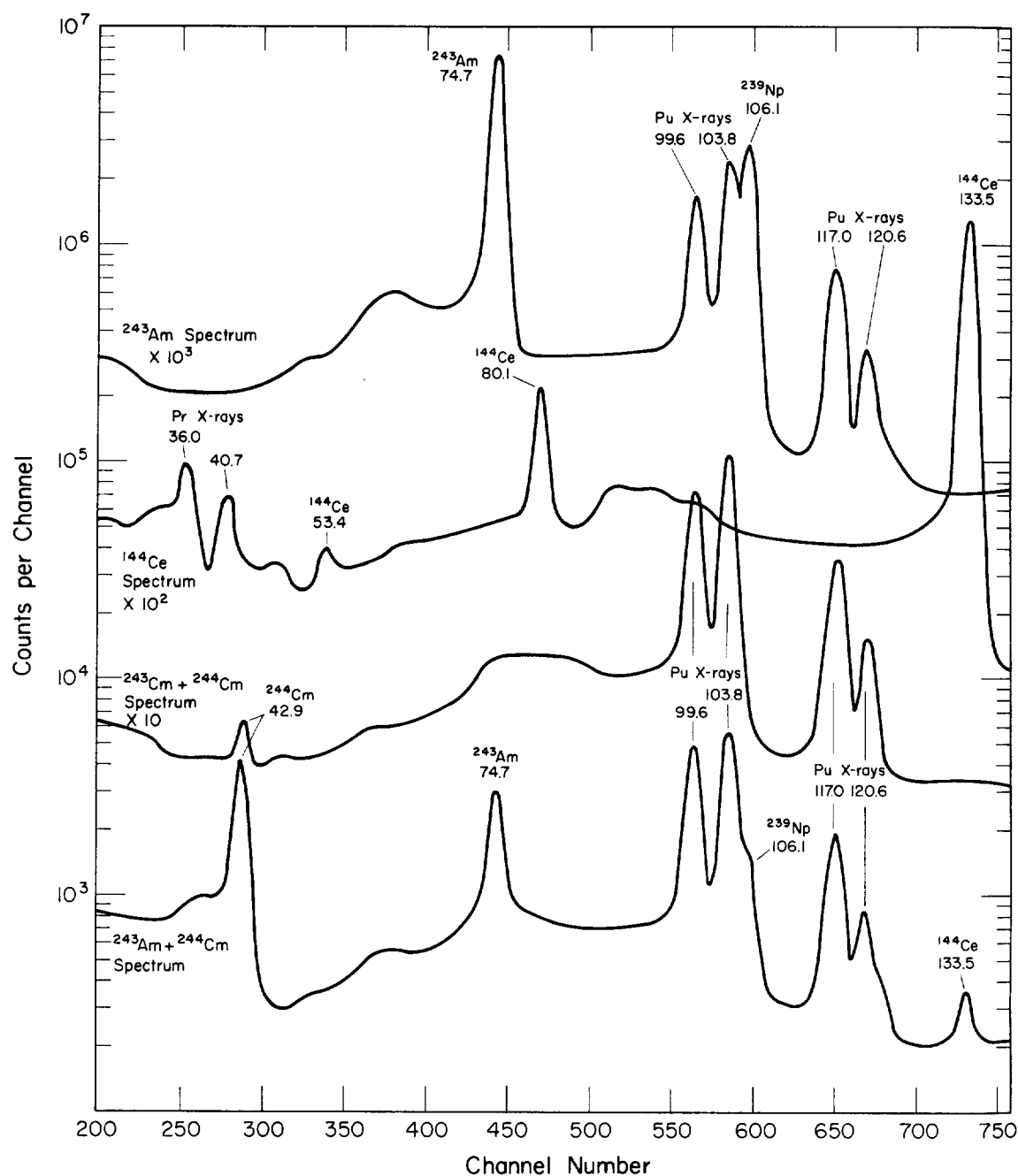|		Rel Std Dev, %	^{243}Am, mg/ml
a.	Replicate results on a standard sample	0.35 (n = 12)	3.70 x 10^{-3}
b.	Repeated analysis of normal sample	1.4 (n = 10)	3.06 x 10^{-3}
c.	Sample with ^{144}Ce and ^{243}Cm interferences	4.5 (n = 10)	6.98 x 10^{-3}
d.	Same sample as c. by ^{239}Np extraction	6.2 (n = 10)	6.95 x 10^{-3}

FIG. 1 Ge (Li) SPECTRA OF NUCLIDES OF INTEREST IN THE DETERMINATION OF ^{263}Am